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## **An algorithm for the regression of the UNIQUAC interaction parameters in liquid-liquid equilibrium for single- and multi-temperature experimental data**

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**Keywords:** Gibbs Common Tangent Plane; UNIQUAC model; Parameter estimation; Liquid-liquid equilibrium; Calculation Method;

### **Abstract**

This paper describes an algorithm for the computation of the UNIQUAC interaction parameters from liquid-liquid experimental data. The algorithm comprises two separate levels. The inner level is devoted to the calculation of the interaction parameters, minimizing an objective function which is function of the activities. The outer level uses the parameters by the inner level and aims to minimize the error between experimental and calculated molar fractions through an adjustment of the experimental molar fractions, provided that the condition of common tangent to the change of the Gibbs free energy of mixing is matched.

The algorithm is applied to seven binary systems for the evaluation of single temperature parameters and to the tetrahydrofuran/water system for the evaluation of the temperature dependent parameters. In both cases, the calculated parameters provide results with lower error than the previously published parameters. In all cases thermodynamically consistent and precise results are obtained in terms of common tangent of the Gibbs free energy of mixing and molar fraction errors.

### **1.Introduction**

The reliability of a thermodynamic model in predicting or correlating phase equilibria depends strongly on the value its parameters. Carefully evaluated parameters enable a more precise calculation of the phase equilibria and of the process units, affecting as a consequence the costs of a process. In several cases, recently developed chemical processes are designed for operating at moderate pressures and temperatures in order to minimize the energy consumption, increasingly facing with liquid-liquid equilibrium (LLE).

Currently, the two most widespread models in use for the description of LLE and vapour-liquid equilibrium (VLE) in such thermodynamic conditions are the UNIQUAC [1] and the NRTL [2] models. Even if both models are widely used since few decades it is impossible to make a clear suggestion which model should be considered with a priority when new data has to be handled. The main advantage of the UNIQUAC lies on its links with the UNIFAC [3] being widely used for prediction of VLE and LLE. In addition the UNIQUAC model involves some molecular property (Q and R) with more substantial contribution for strongly asymmetric systems.

However, in several cases the UNIQUAC model predicts weakly a phase equilibrium because of the values of the interaction parameters which are used within the computation. Evident proofs on that are given by the application of the method proposed in [4] for the evaluation of the model parameters, which is based on the maximum likelihood (ML) principle. This method was

successfully applied to the Van Laar model and successively to the NRTL [5, 6] and UNIQUAC [7] models. The method applies the ML principle to manage the experimental scattering of the experimental data on which the parameters are evaluated. The method leads to the definition of a confidence region (confidence ellipse) where the parameters can span. ML represents a valuable tool to check the effect of the change in parameters on the error between experimental data and calculated values [8].

In this paper we considered the UNIQUAC model in its original version [1] believing that developed algorithm may be applied to the corrected versions of the original UNIQUAC model [9, 10] and NRTL model, for LLE and vapour-liquid-liquid equilibria (VLLE) correlation. A number of algorithm have been proposed in literature to evaluate the binary interaction parameters of thermodynamic models for LLE. A large part of such algorithms neglect the calculation of the isoactivity condition, relying only on the prediction of the correct concentrations [5, 6, 11-13]. The risk of using such algorithms is in generating potentially inconsistent parameters for LLE. This was highlighted by Garcia-Sanchez et. al., [14] and Marcilla et. al., [15], who claimed the necessity of achieving a higher thermodynamic consistency in the parameter evaluation algorithms.

For this reason, hereafter we shall neglect these algorithms, and compare the results exclusively with published algorithms which include an evaluation of the isoactivity condition. Such algorithms are summarised as:

- 1) Britt and Lueke [16]: here the ML principle is applied, considered as a squared objective function. Interaction parameters and independent molar fractions are considered as variables to be optimized. The isoactivity conditions on all the components are introduced as constraints of the minimization problem. This algorithm is further adopted in Aspen Plus [17];
- 2) Sorensen et. al. [18]: the parameter estimation method used in this work involves the minimization of an objective function based on the squared difference between experimental and calculated molar fractions. An objective function based on activities was also introduced as an alternative, but in the end of the investigation the authors recommended the use of objective functions based on molar fractions. The parameters are changed iteratively until minimization of the objective function;
- 3) Sorensen and Artl [19]: The parameters presented here have been calculated considering several binary systems. The system of nonlinear equations, involving the isoactivity conditions  $a_1^I = a_1^{II}$  and  $a_2^I = a_2^{II}$ , was solved iteratively changing the value of the parameters and checking the sign of second derivative of the change in Gibbs free energy of mixing function ( $\Delta G_{\text{mix}}$ );
- 4) Gmehling et. al., [20]: This algorithm has met greater success mainly due to the development of the Dortmund Data Bank [21] and of the Dortmund Data Bank Software Package [22], which incorporates the algorithm. It represents a reference standard for research involving the UNIQUAC model. Details about the application of the algorithm to the LLE are in [20]. The algorithm uses one objective function consisting on the isoactivity condition written in form of  $\sum_i |a_i^I - a_i^{II}|$  and changes the value of the molar fractions according the K-factor method.

The main drawback of all these algorithms consists of their convergence to a minimum of the objective function without any guarantees that the solution is a global minimum of the Gibbs free energy. For this reason consistency tests are usually applied to the calculated molar fractions, which often are only partially fulfilled [23].

Thermodynamically consistent parameters should enable the calculation of the molar fractions at equilibrium in a way that, using those calculated molar fractions and parameters, the Gibbs free energy should be at its global minimum value. Since Gibbs free energy depends on the value of a

102 set of parameters, Gibbs free energy can be regarded as a parametric function which must be placed  
103 at its lowest level acting on the value of the parameters.

104

105 The main problem behind the inability of the previous algorithms in finding the correct parameters,  
106 concerns the nature of the objective functions involved.

107 These objective functions are multivariate multimodal functions of their independent variables  
108 (including in the variables both the molar fractions and the interaction parameters) and for this  
109 reason local and global optimization algorithms operating on them, must be adequately tuned,  
110 especially in terms of initial points.

111 The convergence to the global minimum ensures the matching with the common tangent plane  
112 criterion [24-26], which should be introduced for the correct estimation of the parameters, following  
113 mathematically the graphical method proposed by J.W. Gibbs [27, 28].

114 The common tangent plane (CTP) of  $\Delta G_{\text{mix}}$  can be found by minimizing the distance between the  
115 tangent planes to  $\Delta G_{\text{mix}}$  and  $\Delta G_{\text{mix}}$ , dealing with the problem of the minimization of the tangent  
116 plane distance function (TPDF). It is not easy to minimize the TPDF when the  $\Delta G_{\text{mix}}$  is calculated  
117 by a strongly nonlinear model, i.e. the UNIQUAC model.

118 Hence the computation of the interaction parameters in activity coefficients models, with particular  
119 attention to the strongly nonlinear UNIQUAC model, for LLE is still an open issue.

120

121 In recent years, notable advances have been achieved and two important algorithms have been  
122 proposed.

123 The first is the Simoni et. al. [29] algorithm, applied only to binary systems. It solves the isoactivity  
124 conditions equations with the interval-Newton method, substituting in the system the temperature  
125 and the experimental molar fractions at equilibrium and solving the system considering the  
126 interaction parameters as unknowns. After the solution of the system, the screening of the calculated  
127 multiple solutions allows the identification of the stable solutions matching the minimum of the  
128 TPDF. This algorithm was applied to NRTL model on single temperature binary system data. The  
129 method has 3 limitations: i) it is not able to manage multi-temperature data; ii) it should be modified  
130 for calculation of multi-component mixtures equilibrium; and iii) it fails in solving the system of  
131 isoactivity conditions when applied to strongly nonlinear models, unless it is highly bounded to a  
132 small neighbourhood of the solution.

133 The first two remarks are overcome by approaching the computation of the parameters in a bilevel  
134 way. A bilevel programming problem is a hierarchical problem where two optimization problems  
135 are organized in a way that the first problem (outer level) is constrained by the second one (inner  
136 level). The outer level minimizes the molar fraction error, while the inner level solves the  
137 isoactivity condition dealing with it as a minimization problem.

138

139 A second algorithm, for the solution of the bilevel problems associated with the computation of the  
140 NRTL model parameters, has been proposed in [30, 31]. This algorithm deals with also the problem  
141 of screening the solutions from the systems of isoactivity conditions by excluding the presence of  
142 additional spurious phases. The algorithm has been applied successfully on a number of liquid-  
143 liquid [30] and vapour-liquid [31] binary systems, showing that the bilevel optimization formulation  
144 provides more consistent parameters and it is a powerful tool to capture the temperature dependence  
145 of the parameters. The only limitations concerns the necessity of adequate bilevel algorithms [32]  
146 which have to be efficient also in solving strongly nonlinear equations [33] like the UNIQUAC  
147 equations.

148

149 The present paper describes an algorithm for the computation of the interaction parameters of the  
150 UNIQUAC model in LLE. The algorithm is applied to single and multi-temperature data of binary  
151 systems. The algorithm involves basic optimization algorithms and approaches the problem as a  
152 bilevel problem. The aim is to demonstrate that adopting the described bilevel algorithm, more

consistent and precise single and multi-temperature parameters can be calculated for the UNIQUAC model.

## 2. Description of the algorithm

The algorithm proposed considers in some extent the possible range of variation of the experimental data, bounding the experimental data in a predefined range. The algorithm is illustrated in the flow chart of Fig. 1 and it can be applied to multi-temperature experimental data of binary liquid systems. The necessary data are the set of experimental molar fractions at several different temperatures. The algorithm is organized in two levels and operates respectively according the following steps:

- 1) The first iteration is performed with experimental molar fractions and temperatures. These values are introduced in the minimization problem of eq.(1), which is solved by the Nelder-Mead algorithm [34]. The solution of eq. (1) is the set of interaction parameters  $\Delta u_{12}$  and  $\Delta u_{21}$ . A first objective function  $OF_1$  is calculated here using the calculated interaction parameters, the experimental molar fractions and the experimental temperatures. It corresponds to:

$$OF_1 = \sum_n^{nd} \sum_i^2 \left| x_{i,exp}^I \gamma_i^I (T_{exp}, x_{1,exp}^I, x_{2,exp}^I, \Delta u_{12}, \Delta u_{21}) - x_{i,exp}^{II} \gamma_i^{II} (T_{exp}, x_{1,exp}^{II}, x_{2,exp}^{II}, \Delta u_{12}, \Delta u_{21}) \right| \quad (1)$$

where  $nd$  is the number of experimental data available, corresponding to the number of different temperatures. This step represents the inner level of the algorithm and it constraints the successive calculation (outer level) to be performed using the interaction parameters calculated in this step.

- 2) The previously calculated parameters are introduced in the following system of nonlinear equations:

$$\begin{cases} x_1^I \gamma_1^I (T_{exp}, x_1^I, x_2^I, \Delta u_{12}, \Delta u_{21}) - x_1^{II} \gamma_1^{II} (T_{exp}, x_1^{II}, x_2^{II}, \Delta u_{12}, \Delta u_{21}) = 0 \\ x_2^I \gamma_2^I (T_{exp}, x_1^I, x_2^I, \Delta u_{12}, \Delta u_{21}) - x_2^{II} \gamma_2^{II} (T_{exp}, x_1^{II}, x_2^{II}, \Delta u_{12}, \Delta u_{21}) = 0 \end{cases} \quad (2)$$

The system is solved with a multiple starting points approach and a quasi-Newton method [35, 36], collecting all the solutions.

- 3) Excluding the trivial solution and the solutions with negative TPDF, the CTP condition is checked on each remaining solution. The CTP condition is considered matched if the two tangents of  $\Delta G_{mix}$  in the solution points, are coincident. Finally, among the remaining solutions, the solution having smallest total absolute deviation by the experimental data is chosen. A second objective function  $OF_2$  is calculated at this point:

$$OF_2 = \sum_n^{nd} \sum_j^{nPh} \sum_i^2 \left( \left| x_{i,exp}^j - x_{i,calc}^j \right| + \left| x_{i,iter}^j - x_{i,calc}^j \right| + \left| x_{i,exp}^j - x_{i,iter}^j \right| \right) \quad (3)$$

where  $nPh$  is the number of phases suggested by the experimental data. In the first iteration the values of  $x_{iter}$  are considered identical to the values of  $x_{exp}$ .

- 4) The procedure is repeated starting again from the point 1) changing the experimental molar fractions in a domain defined by the experimental uncertainty and centred in the experimental data. The new mock molar fractions are changed according to the  $(\mu+\lambda)$ -Evolution Strategy and  $(\mu,\lambda)$ -Evolution Strategy optimization algorithm [37, 38] operating on the following objective function:

$$OF = \sqrt{OF_1 + OF_2} \quad (4)$$

Now the new molar fractions ( $x_{iter}$ ) for the successive iteration are different from the experimental molar fractions ( $x_{exp}$ ). So in the second round and for all the successive rounds the step 1 will be calculated using the set of molar fractions generated by the Evolution Strategy algorithm.

- 5) The algorithm ends when the objective function OF converges to the global minimum.

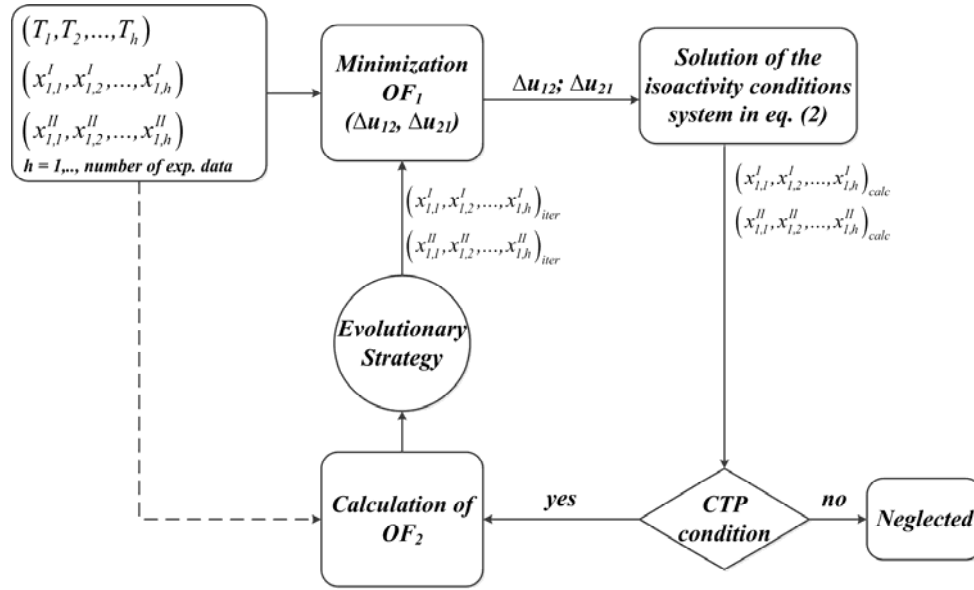


Figure 1: Flow chart of the algorithm used for the calculation of the UNIQUAC interaction parameters

### 3. Results and discussion

#### 3.1. Application of the algorithm to single temperature data

The algorithm described above was used, in a reduced version, for the evaluation of single temperature experimental data. For single temperature data the algorithm ends in step 4, avoiding the iterations changing the molar fraction values and resulting in this way in a single level algorithm.

In [39] has been highlighted how for binary and multicomponent systems, incorrect parameters lead to large errors in molar fractions. Therefore precisely evaluated parameters play a fundamental role in prediction of the experimental data. In order to highlight the limits of the presently adopted interaction parameters, seven liquid-liquid binary systems are considered. No other UNIQUAC binary interaction parameters were proposed in the literature for these systems after the parameters calculated in [19]. Structural parameters adopted in the calculations are reported in Table 1.

Table 1: Structural parameters of the UNIQUAC equation

	R	Q
water	0.92	1.4
methanol	1.4311	1.432
tetrahydrofuran	2.9415	2.72
1-butanol	4.735	3.052
benzene	3.1878	2.4
hexane	4.4998	3.856
n-heptane	5.1742	4.396
1-octanol	6.1519	5.212

Support materials S1-S7 collect the single temperature results of the calculations. The errors are calculated according to eqns. (5) and (6).

$$Isoactivity_i = \left| x_{i,exp}^I \gamma_i^I (x_{1,exp}^I, x_{2,exp}^I, \Delta u_{12}, \Delta u_{21}) - x_{i,exp}^{II} \gamma_i^{II} (x_{1,exp}^{II}, x_{2,exp}^{II}, \Delta u_{12}, \Delta u_{21}) \right| \quad i=I,2 \quad (5)$$

$$x_i^j error = \left| x_{i,exp}^j - x_{i,calc}^j \right| \quad i=I,2; j=I,II \quad (6)$$

In all cases, the literature parameters matched the CTP condition. Support materials S1-S7 show also the values of the parameters when they are computed with high precision and a comparison between the errors respectively adopting the recomputed parameters and the literature parameters. A summary of the results in terms averages on the whole experimental data-set is provided in Table 2.

Table 2: Comparison of the errors adopting published parameters and highly precise parameters. More detailed results are reported in the support materials S1-S7

Binary System (1)/(2)	Molar fraction errors <sup>a</sup>		Isoactivity errors <sup>b</sup>		Molar fraction errors <sup>a</sup>		Isoactivity errors <sup>b</sup>	
	$x^I_{1,error_{old}}$	$x^{II}_{1,error_{old}}$	isoactivity <sub>1,old</sub>	isoactivity <sub>2,old</sub>	$x^I_{1,error_{new}}$	$x^{II}_{1,error_{new}}$	isoactivity <sub>1,new</sub>	isoactivity <sub>2,new</sub>
1-Butanol/Water	$1.56 \cdot 10^{-4}$	$3.10 \cdot 10^{-5}$	$6.10 \cdot 10^{-4}$	$5.21 \cdot 10^{-4}$	$4.44 \cdot 10^{-16}$	$5.42 \cdot 10^{-16}$	$1.20 \cdot 10^{-15}$	$2.96 \cdot 10^{-16}$
Methanol/n-Heptane	$2.18 \cdot 10^{-4}$	$4.81 \cdot 10^{-4}$	$5.21 \cdot 10^{-4}$	$3.51 \cdot 10^{-4}$	$7.51 \cdot 10^{-13}$	$3.20 \cdot 10^{-12}$	$3.92 \cdot 10^{-12}$	$5.20 \cdot 10^{-13}$
n-Heptane/Water	$2.23 \cdot 10^{-6}$	$2.13 \cdot 10^{-9}$	$4.13 \cdot 10^{-3}$	$3.31 \cdot 10^{-3}$	$8.50 \cdot 10^{-16}$	$1.50 \cdot 10^{-16}$	$2.13 \cdot 10^{-13}$	$5.16 \cdot 10^{-13}$
Benzene/Water	$1.12 \cdot 10^{-5}$	$7.73 \cdot 10^{-7}$	$1.69 \cdot 10^{-3}$	$2.96 \cdot 10^{-3}$	$7.66 \cdot 10^{-14}$	$1.05 \cdot 10^{-15}$	$1.66 \cdot 10^{-12}$	$1.48 \cdot 10^{-11}$
Tetrahydrofuran/Water	$3.78 \cdot 10^{-4}$	$1.74 \cdot 10^{-4}$	$1.94 \cdot 10^{-4}$	$8.32 \cdot 10^{-5}$	$5.55 \cdot 10^{-11}$	$1.66 \cdot 10^{-11}$	$1.23 \cdot 10^{-12}$	$5.79 \cdot 10^{-12}$
Methanol/n-Hexane	$1.83 \cdot 10^{-4}$	$3.63 \cdot 10^{-4}$	$6.66 \cdot 10^{-4}$	$3.68 \cdot 10^{-4}$	$6.75 \cdot 10^{-13}$	$1.19 \cdot 10^{-12}$	$3.12 \cdot 10^{-12}$	$1.43 \cdot 10^{-12}$
1-Octanol/Water	$1.54 \cdot 10^{-4}$	$3.54 \cdot 10^{-7}$	$2.50 \cdot 10^{-3}$	$5.37 \cdot 10^{-4}$	$1.89 \cdot 10^{-12}$	$2.70 \cdot 10^{-16}$	$7.76 \cdot 10^{-13}$	$7.26 \cdot 10^{-12}$

Note:

<sup>a</sup> $x^I_{1,error_{old/new}} = (\sum_n |x^I_{1,exp} - x^I_{1,calc}|) / n$  with  $i=1,2$ ; using published/high precision parameters. n=number of experimental data in support material;

<sup>b</sup>isoactivity<sub>1,old/new</sub> =  $(\sum_n |x^I_{1,exp} - x^I_{1,calc}|) / n$  with  $i=1,2$ ; using published/high precision parameters. n=number of experimental data in support material;

Observing the support materials S1-S7, the values of the old parameters and the values of the recomputed parameters are similar, since both the parameters are very close to the centres of the confidence ellipses. Nevertheless a drastic reduction in the errors can be gained both on the isoactivity condition and molar fraction, selecting values of the parameters very close to the confidence ellipses centres. The comparison between old and new parameters suggests that the errors are very sensitive to small changes in the values of the interaction parameters and the problem of the evaluation of the UNIQUAC parameters is ill conditioned. Thus, the precision in the numerical computation is one of the issues affecting the parameters' value and this issue should be carefully handled by whatever kind of algorithm for UNIQUAC parameters computation.

### 3.2. Application of the algorithm to multi-temperature experimental data

The main aspect influencing the precision in the prediction of the experimental data is the a-posteriori regression of the parameters in temperature. Usually, once binary parameters are evaluated in each single temperature, they can be regressed in temperature by linear or nonlinear empirical correlations supposing a trend. A rough a-posteriori regression of the parameters often leads to the increase in errors both in molar fraction and isoactivity conditions, sometimes mismatching for some temperatures with the CTP condition. Indeed, when a nonlinear correlation is adopted, a higher number of regression parameters are introduced, often producing an overfitting model when the number of involved parameters are comparable with the number of experimental data [40]. The case study presented here is the tetrahydrofuran/water binary system. As can be seen in the support material S5, for such system the dependence of the binary interaction parameters by the temperature is nonlinear. After leave-one-out cross validation test, second order polynomial gives lowest errors and thermodynamic consistency. Therefore second order polynomial is adopted in order to take into account the temperature dependence of the interaction parameters. Accordingly, two second order polynomials result in 6 coefficients which can be used to fit the 8 experimental data considered. Table 3 reports the errors in molar fractions and isoactivity conditions adopting nonlinearly temperature-dependent parameters. The correlation in this case is obtained with an a-posteriori regression of the single temperature parameters.

Table 3: Errors adopting a-posteriori temperature-correlated parameters for the binary system tetrahydrofuran (1)/water (2)<sup>a</sup>

T [K]	$x^I_{1,exp} - x^I_{1,calc}$	$x^{II}_{1,exp} - x^{II}_{1,calc}$	$x^I_{1,exp} - x^I_{1,calc}$	$x^{II}_{1,exp} - x^{II}_{1,calc}$
345.25	$2.06 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$	$2.00 \cdot 10^{-4}$	$9.21 \cdot 10^{-5}$
353	$1.20 \cdot 10^{-2}$	$6.18 \cdot 10^{-3}$	$4.30 \cdot 10^{-3}$	$1.96 \cdot 10^{-3}$
363	$7.00 \cdot 10^{-3}$	$2.41 \cdot 10^{-3}$	$3.48 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$
373	$9.85 \cdot 10^{-3}$	$1.35 \cdot 10^{-3}$	$3.41 \cdot 10^{-3}$	$2.21 \cdot 10^{-3}$
383	$1.14 \cdot 10^{-3}$	$1.93 \cdot 10^{-3}$	$2.31 \cdot 10^{-3}$	$5.54 \cdot 10^{-4}$
393	$2.43 \cdot 10^{-3}$	$3.54 \cdot 10^{-5}$	$4.74 \cdot 10^{-4}$	$4.17 \cdot 10^{-4}$
403	$4.64 \cdot 10^{-3}$	$4.14 \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$	$7.93 \cdot 10^{-4}$
409.7	$1.01 \cdot 10^{-2}$	$8.00 \cdot 10^{-3}$	$6.30 \cdot 10^{-4}$	$2.62 \cdot 10^{-4}$
Average	$8.47 \cdot 10^{-3}$	$5.24 \cdot 10^{-3}$	$2.13 \cdot 10^{-3}$	$9.99 \cdot 10^{-4}$

<sup>a</sup> the correlations are:

$$\Delta u_{12} = -1455.04 + 9.7714 T - 0.0150866 T^2$$

$$\Delta u_{21} = -2486.99 + 12.1152 T - 0.0131736 T^2$$

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Comparing the errors in Table 2 with the errors in Table 3, the temperature regression of the interaction parameters increases considerably the errors and for this reason this procedure must be carefully considered to keep low errors.

The main concern on the temperature regression consists of the fact that there are no univocal criteria leading to the selection of the correct temperature dependent correlation. Only the physical interpretation of the change in energy interactions with temperature could provide a reasonable nonlinear dependence [41].

In addition, the weakness of this strategy is also in regressing parameters with heterogeneous errors, distributed heterogeneously on the confidence ellipses. More correctly parameters with homogeneous errors and close to the confidence ellipses centres should be considered in regression. A strategy to reduce the effect of this second concern is to embed the temperature dependence directly in the previously described algorithm. So the task of the algorithm will consist of finding the best coefficients of the correlation. Applying this strategy to the tetrahydrofuran/water binary system, the errors reported in Table 4 are obtained.

Table 4: Errors adopting temperature-correlated parameters for the binary system tetrahydrofuran (1)/water (2) with the correlation embedded in the algorithm<sup>a</sup>

T [K]	$X^I_{1,exp}-X^I_{1,calc}$	$X^{II}_{1,exp}-X^{II}_{1,calc}$	$X^I_1\gamma^I_1-X^{II}_1\gamma^{II}_1$	$X^I_2\gamma^I_2-X^{II}_2\gamma^{II}_2$
345.25	$9.21 \cdot 10^{-4}$	$1.86 \cdot 10^{-3}$	$4.59 \cdot 10^{-4}$	$3.36 \cdot 10^{-4}$
353	$1.16 \cdot 10^{-2}$	$7.51 \cdot 10^{-3}$	$3.84 \cdot 10^{-4}$	$2.88 \cdot 10^{-3}$
363	$3.35 \cdot 10^{-3}$	$1.69 \cdot 10^{-3}$	$7.69 \cdot 10^{-6}$	$4.28 \cdot 10^{-5}$
373	$1.42 \cdot 10^{-2}$	$2.69 \cdot 10^{-3}$	$6.51 \cdot 10^{-4}$	$3.32 \cdot 10^{-3}$
383	$4.95 \cdot 10^{-3}$	$3.44 \cdot 10^{-3}$	$8.22 \cdot 10^{-5}$	$4.35 \cdot 10^{-4}$
393	$3.18 \cdot 10^{-4}$	$1.27 \cdot 10^{-3}$	$1.86 \cdot 10^{-4}$	$1.02 \cdot 10^{-3}$
403	$5.94 \cdot 10^{-3}$	$3.93 \cdot 10^{-3}$	$2.46 \cdot 10^{-4}$	$1.39 \cdot 10^{-3}$
409.7	$1.54 \cdot 10^{-3}$	$3.07 \cdot 10^{-3}$	$2.18 \cdot 10^{-4}$	$3.82 \cdot 10^{-4}$
Average	$5.36 \cdot 10^{-3}$	$3.18 \cdot 10^{-3}$	$2.79 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$

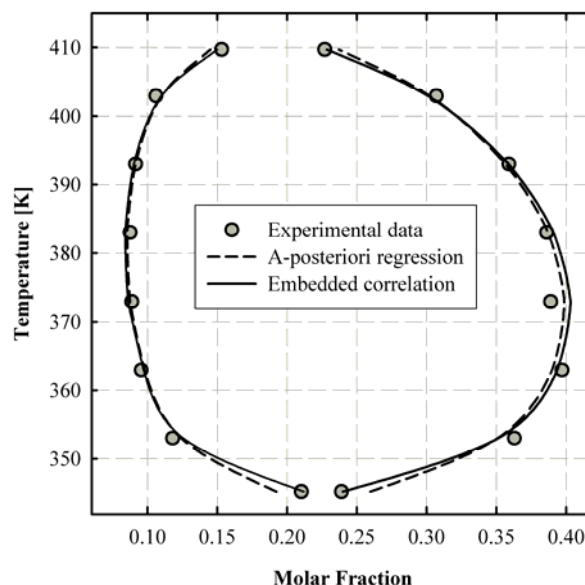
<sup>a</sup> the correlations are:

$$\Delta u_{12} = -1544.38366683089 + 10.3590876766792 T - 0.0160105063588648 T^2$$

$$\Delta u_{21} = -2639.87537303308 + 12.8378043941367 T - 0.0140106377329336 T^2$$

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Fig. 2 compares the experimental equilibrium data for tetrahydrofuran/water in [19] with the values calculated by the a-posteriori regression and using the correlation embedded in the proposed algorithm.



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Figure 2: Prediction of the binodal curve using linear temperature dependent parameters



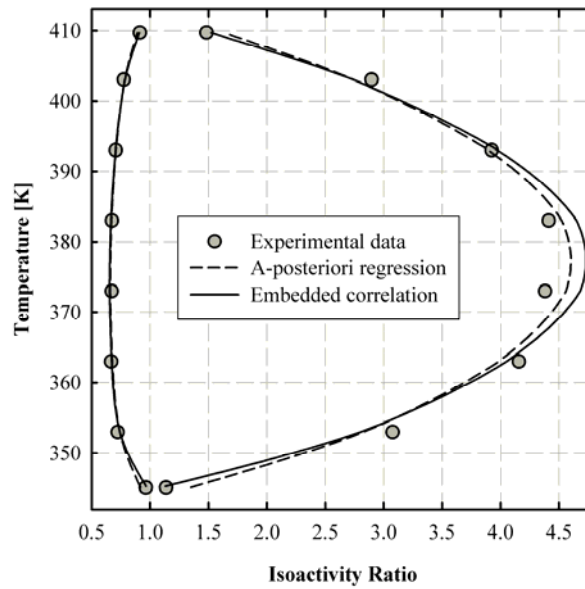
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279 The results show a higher capacity of the proposed algorithm in describing the experimental data  
 280 with a decrease in the average absolute deviations of molar fractions in both phases of 37% and  
 281 39%. The average isoactivity condition decreases of about one order of magnitude for  
 282 tetrahydrofuran and increases of 22% for water. This increase of the error in isoactivity condition of  
 283 water is due to the absence in the original UNIQUAC model of terms to take into account the water-  
 284 water association.

285 Fig. 3 represents the deviations in terms of activity coefficients ratio, adopting the isoactivity  
 286 condition in the form of eq. (7):

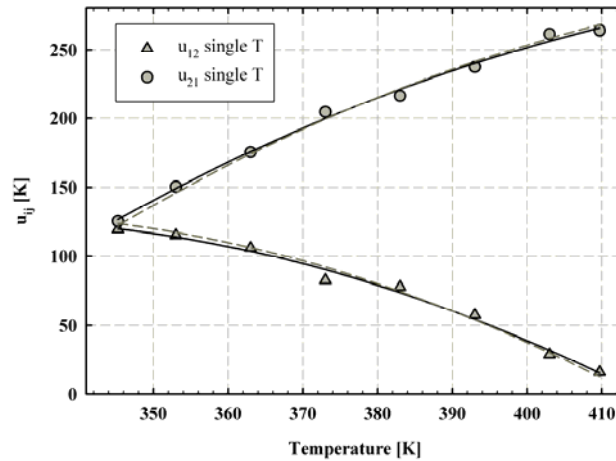
$$287 \frac{x_{i,exp}^I}{x_{i,exp}^{II}} = \frac{\gamma_i^{II}(T_{exp}, x_{1,exp}^{II}, x_{2,exp}^{II}, \Delta u_{12}, \Delta u_{21})}{\gamma_i^I(T_{exp}, x_{1,exp}^I, x_{2,exp}^I, \Delta u_{12}, \Delta u_{21})} \quad i=1,2; \quad (7)$$

288 Fig. 2 and Fig. 3 show that the original UNIQUAC model is able to correlate the  
 289 tetrahydrofuran/water binary system proportionally to the precision of the temperature fitting of the  
 290 parameters. Nevertheless the number of allowed fitting parameters is limited in order to prevent  
 291 overfitting.



292

293 Figure 3: Prediction of the activity coefficients ratio defined in eq. (8), using temperature dependent  
 294 correlations for tetrahydrofuran/water system



295

296 Figure 4: Comparison of single-temperature interaction parameters of the binary system  
 297 tetrahydrofuran(1)/water(2), a-posteriori correlation (solid lines) and optimal correlation (dashed  
 298 lines).

Fig. 4 compares the nonlinear correlations, showing their different trends. Despite the a-posteriori correlation fits at the best the single-temperature parameters, the optimal correlation provides more consistent and precise results. Fig. 5 compares the two different  $\Delta G_{\text{mix}}$  in the cases of single temperature parameters and parameters values calculated adopting the procedure proposed by this paper. In all cases the parameters produce a  $\Delta G_{\text{mix}}$  which shows the presence of two molar fractions having a common tangent. The molar fractions closest to the experimental ones are from single temperature parameters, molar fractions calculated by the a-posteriori fitting of the parameters were worse than those calculated by the embedded correlation.

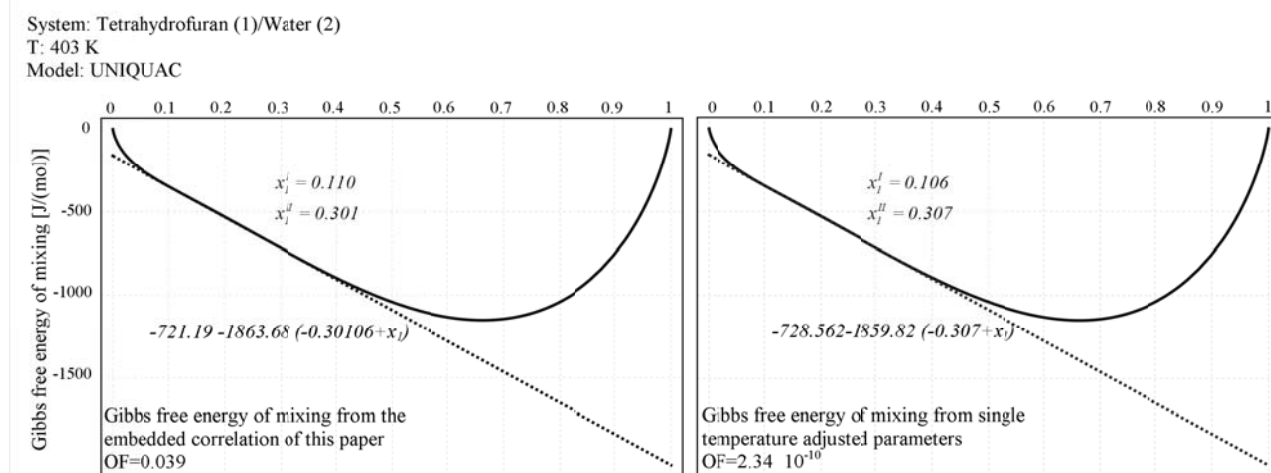


Figure 5:  $\Delta G_{\text{mix}}$  of tetrahydrofuran/water system calculated with UNIQUAC model and different interaction parameters.

The tetrahydrofuran/water system's parameters present a nonlinearity difficult to interpret. There are less challenging systems where the temperature dependence is more easily recognizable, i.e. benzene/water, and adopting the present algorithm, the error values using single temperature parameters can be almost conserved by temperature dependent parameters.

#### 4. Conclusions

Focusing on LLE, a novel algorithm was presented for the precise estimation of the single temperature UNIQUAC parameters and for a more reliable calculation of temperature correlations of the binary interaction parameters. The errors in molar fractions and isoactivity conditions were significantly reduced by the present algorithm compared with previously published values and methods.

The valuable evidences by this work are:

- 1) The errors in molar fraction and isoactivity conditions are very sensitive to small changes in the values of the binary interaction parameters. This means that the problem is ill conditioned;
- 2) The proposed bilevel algorithm produces thermodynamically consistent and highly precise single- and multi-temperature interaction parameters;
- 3) The a-posteriori regression of the single temperature parameters leads always to large errors on the experimental data and on the activities. A reduction of the errors can be gained computing the temperature correlation in the way suggested by the proposed algorithm.
- 4) The model parameters affect the value of the global minimum of the total Gibbs free energy. So instead of only one global minimum, several global minima can be calculated depending on the values of the model parameters. Among the global minima, only the set of parameters collocating the total Gibbs free energy at its lowest level should be considered as solution. This remark claims on the necessity of introducing a thermodynamic consistency check in terms of common tangent of the  $\Delta G_{\text{mix}}$  in the regression algorithm. Adding this check the

338 regression procedure acquire a bilevel nature and ad-hoc algorithms must be applied for  
 339 dealing with the regression task.  
 340 The algorithm presented was applied to the UNIQUAC model but the proposed approach could be  
 341 replicated to other thermodynamic models for LLE.

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### 347 **Nomenclature**

348	R	volume structural parameter;
349	Q	surface structural parameter;
350	x	mole fraction;
351	$\gamma$	activity coefficient;
352	$\Delta u$	energy interaction parameter; [K]. The values of the parameters $\Delta u_{ij}$ are introduced in 353 the UNIQUAC model using the factor $\tau_{i,j}=e^{(-\Delta u_{i,j}/T)}$ . So the value $\Delta u_{i,j}$ already 354 considers the universal gas constant but not the minus sign.
355	T	temperature; [K]
356	OF	objective function;
357	nPh	number of phases;
358	nd	number of data;

### 359 *Subscripts*

360	exp	experimental
361	calc	calculated
362	iter	iteration
363	i	component i
364	old	calculated with literature parameters
365	new	calculated with new parameters

### 366 *Superscripts*

367	I	phase 1
368	II	phase 2
369	j	phase j

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